

Empirical Formula of the Absolute Value of Electrical Conductivity for Elemental Metals and Its Interpretation By Fluctuation Dissipation Theorem

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(Dated: January 20, 2014)

We propose an empirical formula of the absolute values of electrical conductivity σ for pure elemental metals such as Na, Cu, or Fe at room temperature ranges. Assuming the relaxation time of $\tau_0 = \hbar/k_B T$ for all metals, we propose $\sigma = e^2 n_{\text{atom}} \tau_0 / (mG)$ (n_{atom} = number density of atoms in each metal, but not that of electrons n , m = true electron mass). If we adopt that a single free parameter G is the sum of outer electron numbers in electron configuration such as $G = 1 + 2 = 3$ for $\text{In}^{49}(5s^2 4p^1)$, the ‘absolute values’ of σ and the thermal conductivity λ agree with experiments within $\sim 20\%$ for the most of metals, including semimetals (Bi, Sb, and As), and also, only for λ , Si and Ge.

We find that the above results are only compatible with $n = n_{\text{atom}}$ ($Z = 1$) for all metals as far as σ is concerned, and also compatible with $G/\tau_0 = \sum_{i=1}^G (1/\tau_i)$. Here $\tau_i = \tau_0$ is assumed for each i band; e.g. each of two 5s and one 1p bands in Indium. Using the theoretical state density, the electron specific heat ratio $C_{\text{Ve-obs.}}/C_{\text{Ve-theory}}$ leads to $m^*/m \simeq 1$ for 24 metals, supporting use of m (m^* = effective ‘thermal’ electron mass). We derive $\tau_0 = \hbar/k_B T$ by (A)~(C) methods. (A) The Bardeen’s (1937) τ is reduced to τ_0 by adopting an empirically ascertained relation of the acoustic and Fermi energy, though requiring the deformation potential equal to the Fermi energy. (B) Assuming that $1/\tau = n_{\text{eff}} S V_F$ (V_F = Fermi velocity, S = collision area), and n_{eff} is the effective number density of colliding electrons due to the Fermi-distribution saturation, we can reproduce τ_0 . (C) To obtain τ_0 , the fluctuation-dissipation theorem is found to require $\int \frac{1}{2} m < v(0)v(t) > dt = < \Delta E > < \Delta t > = \hbar/2$. Here $v(t)$ is the fluctuating electron velocity around the Fermi velocity. This $\hbar/2$ is the Heisenberg’s minimum uncertainty value, related to the minimum wave function, which in turn is realized by free electron motions suggested by very large mean free paths in metals. The version (C) needs no parameters and seems a most reliable.

PACS numbers: 72.15Eb, 72.15Lh, 72.10.Bg, 65.40.Ba

1. Introduction

In this paper we treat only elemental metals such as Na, Cu, Fe, etc. without impurity and in the room temperature range. We study metals of normal geometrical size at standard pressure. Conventional formulae [1–3] for the electrical conductivity σ and thermal conductivity λ in the free electron model are $\sigma = (\tau n / m^*) e^2$ and $\lambda = (\tau n / m^*) \pi^2 k_B^2 T / 3$, respectively. Here τ is the relaxation time of electrons at the Fermi energy E_F , m^* is the effective electron mass and n is the electron number density of metals, satisfying $n = Z n_{\text{atom}}$, where n_{atom} = metal density/atom weight [m^{-3}]. In order to derive ‘the absolute values’ of σ and λ one needs to know τ , Z and m^* , all of which are poorly known for many metals, especially τ , if not from the observations.

For example, we note that $\tau \sim \hbar/k_B T$ was claimed for $T \gg \Theta$ [4, 5] and Abrikosov [5] extends to use it also for $T \approx \Theta$ as in eq.(4.18) (see foot note therein). Here Θ is the Debye temperature. The accuracy of the ‘tilde’ signs they used is, however, not clear, but also they did not treat multivalent metals. Pippard [6] holds a high opinion of the 1937-Bardeen [7] calculation for monovalent metals on the absolute σ value of Na and K, while Ziman [8] expressed that it is not very accurate, probably because of a factor of two to three difference between experiments of σ_{obs} and the Bardeen theory for Rb, Cs, Cu, Ag, and Au, where $\sigma \propto (E_F/C)^2$. Here C is the deforma-

tion potential. A concise derivation of the relaxation time $\tau \equiv 1/W$ is in Kittel [3] (Appendix J) which still needs values of C , m^*/m and the sound speed. Here again no statements are made on multivalent metals. Certainly, there have been attempts to relate σ to electronic configuration early in 1950’s e.g. by Gerritsen[9], but combination of parameters are unlike the present ones, which are G and n_{atom} as shown below; namely these attempts were effectively unsuccessful.

This paper is organized as follows. Section 2 presents our formulae for σ and λ . Section 3 compares the experimental values with our formulae, by assigning the single parameter G of the sum of outer electron bands in each atom. Sections 4-8 inspect if the assumptions made in Sect.2 are feasible. Section 4 finds $n = n_{\text{atom}}$, namely $Z = 1$, for all elemental metals (not for alloys), though n -values were not needed in Sects.2 and 3, and discusses the role of G in the macroscopic momentum equation. This $Z = 1$ is applicable only for σ and λ . Section 5 finds that $m^*/m \simeq 1$ is also consistent with the electron specific heat expected from the theoretical Fermi energy. Section 6 finds that the τ -value given by Bardeen [7] is reduced to $\tau_0 \equiv \hbar/k_B T$ if an empirically ascertained relation of $3MC_s^2 \approx E_F$ is employed, which resembles the Bohm-Staver relation (M = ion mass and C_s = total sound speed). Section 7 derives an approximate value of τ_0 from $\tau^{-1} = n_{\text{eff}} S V_F$ ‘without explicitly introducing ion thermal vibrations’. Here $n_{\text{eff}} \propto n \frac{k_B T}{E_F}$ is the effective

number density of electrons in the Fermi distribution, S is the collision cross-section and V_F is the Fermi velocity. Section 8 adopts that $\sigma = ne^2 \int_0^\infty \langle v(0)v(t) \rangle dt / k_B T$ from the classical fluctuation dissipation theorem of Kubo[10] is equal to σ from the Drude form ($v(t)$ is the fluctuating electron velocity), and then finds that in order to reproduce $\tau_0 = \hbar/k_B T$, $\frac{1}{2}m \langle v^2 \rangle \Delta t = \hbar/2$ should hold, claimed earlier by the present author[11]. Since electrons in metals are considered to behave as free electrons as judged from the large mean free paths, their wave functions will take the minimum uncertainty Gaussian form so that the minimum uncertainty relation will hold, consistent with the requirement from the observations. Section 9 is the discussion and Sect.10 is the summary. Appendix gives the standard derivation of the Drude formula from the Boltzmann equation with some discussions.

2. Formulae We Propose

In this paper we give these absolute values which are in good accord with the observations by adopting assumptions below. We assume for ‘all’ elemental metals

$$\tau_0 = \hbar/k_B T, \quad (1)$$

and introduce a non-dimensional parameter G (integer) in place of the conventional $m^*/(mZ)$ appearing in the Drude formula. We then propose, using n_{atom} instead of the electron density n ,

$$\left(\frac{\sigma}{\lambda} \right) = \frac{e^2 n_{\text{atom}} \tau_0}{m} \frac{1}{G} \left(\frac{1}{\pi^2 k_B^2 T / (3e^2)} \right). \quad (2)$$

Here σ is in $\Omega^{-1}\text{m}^{-1}$, λ is in $\text{Wm}^{-1}\text{K}^{-1}$, $\hbar = h/2\pi$ (h is the Planck constant), k_B is the Boltzmann constant, and e is the elementary charge (positive value).

These two equations, Eqs.(1) and (2) ‘combined’, do not seem to have been proposed in the past. Note that Eq.(2) gives $\sigma \propto 1/T$ due to $\tau_0 \propto 1/T$ and temperature ‘independent’- λ both being consistent with observations in the room temperature range (‘independent’ means as compared to $\sigma \propto 1/T$ variation). Since n_{atom} for each metal (from density and atomic weight) and T can be given, the only non-dimensional parameter is G . Even if τ is different from Eq.(1), unknown departure factor from it can be included in G (e.g. m^*/m or deformed potential in a non-dimensional constant). Thus assuming $\tau_0 = \hbar/k_B T$, we first empirically determine the parameter G_{obs} using observed σ_{obs} for each metal. Then we assign G (guessed)-values to be the sum of the outer electron numbers in electron configuration which are ‘close’ to G_{obs} .

3. Comparison with Experiments

Figure 1(a) presents G_{obs} plotted against ‘group’ number for each ‘period’ in the periodic table. Here G_{obs} is

defined as

$$G_{\text{obs}} \equiv \frac{\sigma_1}{\sigma_{\text{obs}}} \quad \text{and} \quad \sigma_1 \equiv \sigma(G=1) = \frac{e^2 n_{\text{atom}}}{m} \frac{\hbar}{k_B T}. \quad (3)$$

Then G_{obs} can be given for each metal from σ_{obs} , n_{atom} and temperature T used in the observations. Observed values (σ_{obs} and λ_{obs}) for 48 metals are taken from Kittel[3], adding $1/\sigma(\text{As}^{33})=333\text{n}\Omega\text{m}$ and $\lambda(\text{Ca})=201\text{Wm}^{-1}\text{K}^{-1}$ from the table of Phys. Soc. Japan [12] (PSJ-table). We adopt $T_{\text{obs}}=295\text{K}$ from the Kittel’s tabulation for σ_{obs} . This gives $\tau_0 = 2.59 \times 10^{-14}\text{s}$ from Eq.(1), which is very close to τ_{obs} from the observed σ_{obs} such as $\tau_{\text{obs}}(\text{Na})=2.9 \times 10^{-14}\text{s}$ and $\tau_{\text{obs}}(\text{Cu})=2.5 \times 10^{-14}\text{s}$, using Eq.(2) for $G=1$.

First, we find similar trends of G_{obs} among periods of 4 ($\text{K}^{19}-\text{Ga}^{31}$), 5 ($\text{Rb}^{37}-\text{Sb}^{51}$), and 6 ($\text{Cs}^{55}-\text{Bi}^{83}$, inclusive of La^{57}). This suggests that electron configuration, which is the basis of the periodic table, may be responsible (see e.g. early attempts in Figs. 12-13 by Gerritsen [9]). Secondly, $G_{\text{obs}} \approx 1$ is found for Na^{11} , K^{19} , Rb^{37} , Cs^{55} , and noble metals of Cu^{29} , Ag^{47} , and Au^{79} . This indicates that Eq.(2) for the electrical conductivity σ with $G=1$ agrees with the observations without further parameters (Fig. 1(b)-upper). These seven elements in free atomic form have each $3s^1 - 6s^1$ outermost electron. Though one might say that $Z=1$ and $m^*=m$ hold as expected, τ_0 should be specified as we propose.

Third, many metals appear concentrated in $G_{\text{obs}} = 1$, 3, 5 and 10 – 13, which suggests discreteness of $1/\sigma_{\text{obs}}$ if expressed in unit of $1/\sigma_1$, namely the true G may well be quantized!

Further we find that in the Kittel’s periodic table (K-P-table; in the back cover of the book), not necessarily in other authors’ tables, sum of numbers in the outer electronic configuration matches the observed G_{obs} quite well. In fact we find that besides $G \approx 1$ (from $G_{\text{obs}} \approx 1$) for s^1 -electron atoms, $G=3$ (from $G_{\text{obs}} \approx 3$) for 3-outer-electron atoms as in $\text{In}^{49}(5s^2 5p^1)$, and $G=5$ for 5-outer-electron atoms as in $\text{Nb}^{41}(4d^4 5s^1)$. Other examples besides $G=1, 3$ and 5 are $\text{Mg}^{12}(3s^2 \rightarrow G=2)$, $\text{Cr}^{24}(3d^5 4s^1 \rightarrow G=6)$, $\text{Zn}^{30}(4s^2 \rightarrow G=2)$, $\text{Tc}^{43}(4d^5 5s^2 \rightarrow G=7)$; not $4d^6 5s^1$ as in the K-P-table), and $\text{Pb}^{82}(6s^2 6p^2 \rightarrow G=4)$. These estimated G -values are shown in Fig. 1 in the top and bottom. While the K-P-table actually lists as $3d^{10} 4s^2$ for Zn, we ignore $3d^{10}$, as we ignore the same $nd^{10}(n=3-5)$ in Cu, Ag, Au, and $\text{Cd}^{48}(5s^2 \rightarrow G=2)$: if we added 10 to G , σ would become much less than the observation, though nd^{10} may be important for the electronic structure. In the case of Cu, we know that the state density from d^{10} -bands is confined below the Fermi energy and hence no contribution (see Fig. 7.12 of Ibach and Lüth[2]). We add further $\text{Al}^{13}(G=1, \text{ only } 2p^1 \text{ is used instead of usual } G=3 \text{ from } 2s^2 2p^1, \text{ since } G_{\text{obs}}=1.2)$, Sr^{38} , Ta^{73} , $\text{W}^{74}(G=2, 6s^2)$, Re^{75} , $\text{Ir}^{77}(G=2 \text{ from } 5d^7 6s^2, \text{ but not } 5d^9 \text{ as in the K-P-table})$, and Tl^{81} . Altogether 22 metals in the K-P-table show that if one uses these G -values, Eq.(2) holds quite well with the scatter rms of

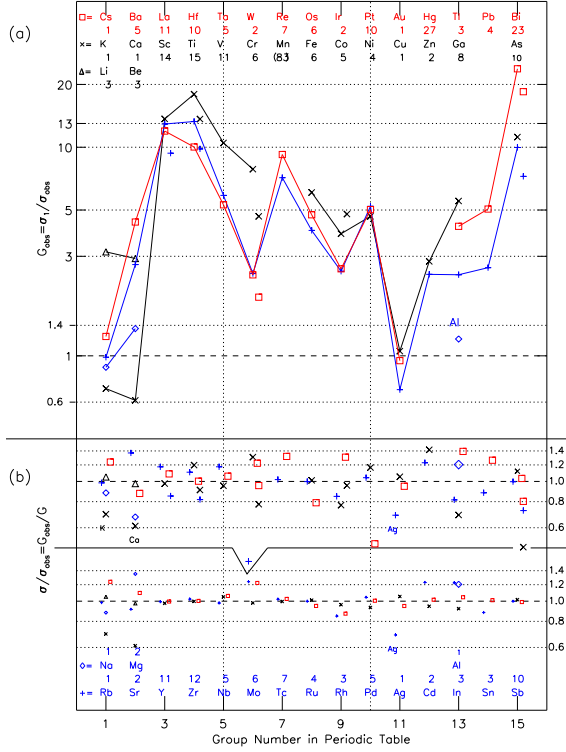


FIG. 1: (color online) (a) $G_{\text{obs}} \equiv \sigma_1/\sigma_{\text{obs}}$ and (b) $G_{\text{obs}}/G = \sigma/\sigma_{\text{obs}}$ against group number for each period, both in the same logarithmic scales. Thick marks in (a) and (b)-upper are $\lambda_1/\lambda_{\text{obs}}$ values for eight metals with $|C_{\text{WF}} - 1| > 0.2$ (see text; As³³ for λ is not shown since the ratio of $G_{\text{obs}} - \sigma = 11.2$ and $G_{\text{obs}} - \lambda = 4.9$ is too large for plotting). Horizontal positions for some metals are slightly shifted to avoid overlapping. Numerals in the top and bottom are adopted G -values.

$$|G_{\text{obs}} - G|/G = |\sigma - \sigma_{\text{obs}}|/\sigma_{\text{obs}} = 23\%.$$

For the remaining 26 metals, we need to inspect in detail, primarily because the periodic table itself is rather complicated. There seem two ways of guessing G . In the first method, given the observed G_{obs} , we force to choose configurations counted from the highest term until the sum of electron numbers becomes closest to G_{obs} , that is we round off G_{obs} to integer such that $|G - G_{\text{obs}}| \leq 0.5$, namely $G \equiv (G_{\text{obs}})_{\text{round}}$. Naturally G/G_{obs} becomes almost unity as seen in Fig. 1(b)-lower. Though in principle there seems no reason to reject this first method which entirely ignores the electron configuration such as $3d^5 4s^2$, we ‘feel uneasy’ because many metals show much smaller deviations from unity than the relative differences of ‘non-identical experimental σ -values’ between the K-P-table and PSJ-table ($\pm 7\%$ for 38 metals).

We adopt then an alternative second method in this paper as shown below. We add deeper ‘electron configurations’ (hereafter E-config) for some elements than the K-P-table; examples are Li³ (from $2s^1$ to $\underline{1s^2 2s^1}$, leading to $G = 3$), V²³ ($3d^3 4s^2 \rightarrow \underline{3p^6 3d^3 4s^2} \rightarrow G = 11$), and

Bi⁸³ ($6s^2 6p^3 \rightarrow 5s^2 5p^6 5d^{10} 6s^2 6p^3 \rightarrow 23$). Here the added part is underlined. The last one Bi a typical semimetal, may be noteworthy, where $1/\sigma_{\text{obs}} \equiv \rho_{\text{obs}} = 1160 \text{ n}\Omega \text{ m} \approx 1.5 \rho_{\text{obs}}(\text{La}^{57})$ at 300K. This is because by including enough deep levels, it can be treated in the same way as others, and Bi gives $\sigma \approx \sigma_{\text{obs}}$ using $G_{\text{obs}} = 23.8$ (full E-config of Bi⁸³ is $\{\{\text{Pd}^{46}\} 4f^{14}\} 5s^2 5p^6 5d^{10} 6s^2 6p^3$). We could have assigned $G = 21$ by excluding the first $5s^2$, indicating non unique G -values for a large G_{obs} . A brief comment is given for semimetals near the section end. Adding Y³⁹ ($G=11$), Zr⁴⁰ ($G=12$), La⁵⁷ ($G=11$), and Hf⁷² ($G=10$ from $5p^6 5d^2 6s^2$, not $4f^{14} 5d^2 6s^2$ as in K-P-table), seven metals fall in this category (altogether 29 metals up to this point).

Though it is possible to treat Sc, Ti and iron group similarly, we introduce two rules below to obtain ‘much better’ agreements with the observations. We first introduce what we call (10- x)-rule. We examine Fe²⁶ (listed as $3d^6 4s^2$ in the K-P-table), Co²⁷ ($3d^7 4s^2$) and Ni²⁸ ($3d^8 4s^2$), giving ‘tentative’ values of $G_{\text{tent}} = 8, 9$ and 10 , respectively. However if we introduce one rule that if $G_{\text{tent}} > 5$ is encountered in d-band where the saturation is 10, we use $G = 10 - G_{\text{tent}}$ as a subset of d-band. Then G/G_{obs} becomes closer to unity. Namely, $G_{\text{obs}} = (6.1, 3.8, 4.7)$ and new $G = (2+4, 2+3, 2+2)$ are obtained for Fe, Co, and Ni, respectively, where the first numeral 2’s come from s^2 . The result is $G/G_{\text{obs}} = \sigma_{\text{obs}}/\sigma = (6/6.1, 5/3.8, 4/4.7) = (0.98, 1.3, 0.85)$. On the other hand for G_{tent} we would have obtained $G_{\text{tent}}/G_{\text{obs}} = (1.6, 2.9, 2.6)$, which we regard unsatisfactory. We applied this rule altogether to six elements in 8th – 10th group, including Ru⁴⁴, Rh⁴⁵, and Os⁷⁶.

This kind of rule is seen in atomic spectroscopy [13, 14], where d^x and d^{10-x} give the same LS coupling terms such as $^1S, ^1D, ^1G, ^3P$, and 3F for $x = 2$ together with similar rules like p^{6-x} and f^{14-x} , being called ‘equivalent’ electrons for the same set of (n, l) . Also when the cohesive energy of many metals was estimated, a similar kind of rule has been utilized [15], which is broadly consistent with an extensive calculation [16]. The only strong reason however that we use (10- x)-rule is because it gives better agreements with experiments.

Finally we introduce what we call (1/2)-rule. When the G_{obs} -value in a metal corresponds just inside of semi-closed shells of $g=2, 6$ or 10 (statistical weight), we take 1/2 of these values to the last of the sum of E-config. This is a sort of extended (10- x)-rule. Underlying presumption is that though these 2, 6 and 10 electrons are closely packed, there might be weak breaks just in the middle of these, namely 1, 3 and 5. As a first example, Pd⁴⁶ ($4d^{10}$) shows $G_{\text{obs}} = 5.2$ for σ , hence instead of adopting $G = 10$, we adopt $G = 5$ from $10/2$. We applied the ‘1/2-rule’ also for Ca²⁰ ($4s^2, G=1, G_{\text{obs}}=0.6$; instead of usual $G = 2$), and Sn⁵⁰. For six metals we combine the addition of deeper terms to the K-P-table and the ‘1/2-rule’; Sc²¹ ($\underline{2p^6 3s^2 3p^6 3d^1 4s^2} \rightarrow G = 14$), Ti²² ($\underline{2p^6 3s^2 3p^6 3d^2 4s^2} \rightarrow G = 15$) and Ba⁵⁶ ($\underline{5p^6 6s^2} \rightarrow G = 5$). Here added terms are underlined, and 6 in

2p⁶-bands (Sc and Ti) or 5p⁶-bands (Ba) is replaced by 6/2=3. Also Be⁴($G=3$), Ga³¹($G=8$) and Sb⁵¹($G=10$) fall in this group. Again it is noteworthy that though Sb is a semimetal, it can be treated in the same way as the usual metal; namely $G=10$ for Sb⁵¹, almost identical to $G_{\text{obs}}=10.0$, comes from an addition of 5 from K-P-table (5s²5p³) and 5=10/2 (1/2-rule for 4d¹⁰) from full E-config of Kr³⁶4d¹⁰5s²5p³. Note that the resistivity of Sb ($1/\sigma_{\text{obs}}=413\text{n}\Omega\text{m}$) is similar to that of Sc, Ti, or Zr. Further, another semimetal As³³ (Ar¹⁸3d¹⁰4s²4p³) shows $G_{\text{obs}}=11.2$ ($1/\sigma_{\text{obs}}=333\text{n}\Omega\text{m}$ from PSJ-Table[12]) so that $G=10$ (1/2-rule for 3d¹⁰) may be appropriate.

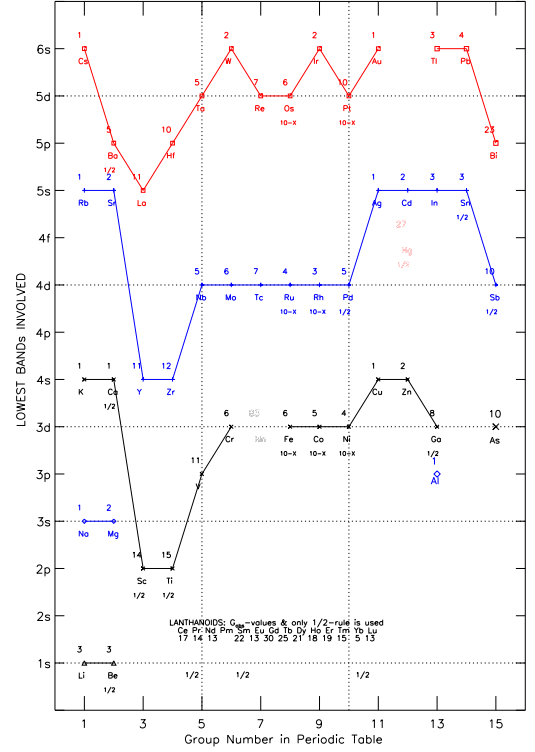
Although use of ‘(1/2)-rule’, so far applied to ten metals, is due primarily to better fit the observations, we want to stress that without this rule $|G - G_{\text{obs}}|/G_{\text{obs}}$ would become much larger than in other metals in the same group where these rules are not needed (see Fig. 2).

The remaining four metals are problematic in one way or another: Mn²⁵($G_{\text{obs}}=83>25$ of atomic number, but see Fig.26 of Meaden [17]), Mo⁴²($G_{\text{obs}}=2.5$; $G=1$, though 5 is possible), Pt⁷⁸($G_{\text{obs}}=5.0$, $G=9$, though $G=2$ is possible), and Hg⁸⁰(liquid; $G_{\text{obs}}=28.5$ and $G=27$).

Figure 1 (b)-upper shows, excluding the problematic four metals above, an rms scatter of $\pm 20\%$ which is larger than the observation error of $(\text{rms})_{\text{obs}} = \pm 7\%$ mentioned before. This suggests that the scatter stems largely from not-yet incorporated causes $[(\text{rms})_{\text{obs}} = \pm 14\%$ for $G = (G_{\text{obs}})_{\text{round}}$ in Fig. 1(b)-lower].

For the thermal conductivity λ , we also show $G_{\text{obs}-\lambda} \equiv \lambda_1/\lambda_{\text{obs}}$ [Fig. 1(a)] and $\lambda/\lambda_{\text{obs}}$ [Fig. 1(b)-upper] in thick marks [$\lambda_1 \equiv \lambda(G=1)$]. Here we employed Eq.(2) for λ with the same G used for σ . We plotted only nine metals showing large departure from the Wiedemann-Franz law[1–3] ($|C_{\text{WF}} - 1| \geq 0.2$): Ti, Cr, Co, As, Y, Zr, Sb, W, and Bi. Here $C_{\text{WF}} \equiv \lambda/(\sigma T L_z)$, where $L_z \equiv \pi^2 k_B^2/3e^2$. We find no appreciable differences from $G_{\text{obs}} = \sigma_1/\sigma_{\text{obs}}$ even for those metals of large $|C_{\text{WF}} - 1|$ (though in As it is rather large).

Figure 2, which is supplementary to Fig. 1, shows that the position of estimated G ’s in E-config. For example, E-config of Fe²⁶ is Ar¹⁸3d⁶4s² and we adopted $G = 2 + 4 = 6$ (4 comes from $10 - 6$ in d⁶) added from outer ones, where 4 is within the 3d-band. Hence for Fe we plotted at 3d. Fig. 2 shows rather systematic behavior, particularly among 4-6 periods (starting from K, Rb, and Cs). This indicates that our choice of G , though adopted only to match the observations, appears to be rooted from some physical basis. In fact we notice that groups 3-4 (Sc²¹, Ti²², Y³⁹, Zr⁴⁰, and La⁵⁷), which stem deeper configurations than other metals, all have configurations where electrons are filled in the outer bands before inner bands become filled up or closed; e.g. Sc²¹= {Be⁴}2p⁶3s²3p⁶3d¹4s² instead of {Be⁴}2p⁶3s²3p⁶3d³, while the 3d-orbit only saturates at Cu²⁹ as 3d¹⁰. This is of course typical characteristics of the earlier transition elements. It might suggest some unstableness of so to speak *heavier upper floors* than e.g.



bulk modulus, and cohesive energy, we can find metals showing similar values. The only difference seems to be the lattice structure of ‘rhomb’ of semimetals in Kittel’s tabulation.

The very small density n_e (e.g. observed from the Hall effect in the magnetic field of $B = 10^4$ G) is expressed[18, 19] as $n_e(B \neq 0)/n = (\Delta E_e/E_F)^{1/2} \det \mathbf{m} \ll 1$ in unit of the total electron density n . Here \mathbf{m} is the diagonal mass tensor in m unit, and ΔE_e is the difference between the Fermi energy and extremum energy for electrons. Both factors, “the determinant of \mathbf{m} ” and $(\Delta E_e/E_F)^{1/2}$, are known much smaller than unity. Therefore as far as σ and λ at T_{room} without magnetic fields are concerned, they behave as if $\det \mathbf{m} = 1$ ($m^* = m$) and $\Delta E_e/E_F = 1$ were to hold, and hence in this empirical paper, it may be allowed to say that semimetals can be treated similarly as ordinary metals.

Below is an extra note for the semiconductor. It is well-known that the thermal conductivities of Si¹⁴ and Ge³² are not much different from ordinary metals, unlike much reduced electrical conductivity due to the gap of ~ 1 eV; namely $\lambda_{\text{obs}}(\text{Wm}^{-1}\text{K}^{-1}) = 148(\text{Si}) \approx 147(\text{Ir})$ or $\lambda_{\text{obs}} = 60(\text{Ge}) \approx 58(\text{Rb})$ at 300 K. Thus assigning similarly G to them, we find that Si ($\text{Ne}^{10}3s^23p^2$) shows $G_{\text{obs}-\lambda} = 1.78$ and $G = 2$ from $2p^2$, giving $\lambda/\lambda_{\text{obs}} = 0.89$, and Ge ($\text{Ar}^{18}3d^{10}4s^24p^2$) shows $G_{\text{obs}-\lambda} = 3.90$ and $G = 4$ from $4s^24p^2$, giving $\lambda/\lambda_{\text{obs}} = 0.98$; satisfactory results in selecting G by reasonable E-config too.

4. $Z=1$ is Expected in All Metals for σ

Though Eq.(2) needs only values of n_{atom} , naturally we wish to know n or $Z \equiv n/n_{\text{atom}}$. This Z value is tabulated only for 20 metals in Kittel’s table [3], while the other quantities are tabulated for almost all metals, indicating that to assign Z -value is not easy. This means in turn that there is no reliable theory how to assign Z for electrical conductivity, so that we search empirically for Z in multivalent metals. Below we use the letter ‘ Z' ’, emphasizing so-called valence electron numbers only applicable to electrical conductivity of elemental metals σ , i.e. not for alloys. We also assume that Z_σ is equal for thermal conductivity and possibly at all temperature range.

The result of Sect.2 indicates that there seems no room for $Z_\sigma \neq 1$, because $\sigma = Z_\sigma \times n_{\text{atom}} e^2 \tau_0 / (mG)$ with $\tau_0 = \hbar / (k_B T)$ and G listed in Figs. 1-2 cannot reproduce the observations. In other words, the fact that we can reproduce the observation quite well without knowing Z_σ -value suggests by itself already $Z_\sigma = 1$. Namely

$$Z_\sigma \equiv n/n_{\text{atom}} = 1 \quad (4)$$

is expected for the majority of elemental metals in electrical and thermal conductivities, if not for e.g. cohesive energy and compressibility, or if not for alloys. [Note that Z_σ and G are different physical quantities. The G is the number of bands ‘responsible’ for σ for ‘a single electron’, which is only one per atom in the elemental metal

as expressed $Z_\sigma = 1$ (here the word ‘responsible’ means that the state density $D(E)$ for that band shows non-zero values beyond the Fermi energy; see Appendix).]

Nevertheless we inspect Z -values using two options below. In both cases we assume $\tau_i = \tau_0 = \hbar / k_B T$ of Eq.(1) for each i -band, and the sum of the number of band is equal to G , namely $\sum_{i=1}^G 1 = G$. Let us first assume that the total resistivity for multi-band metals is given by

$$\rho \equiv 1/\sigma = \Sigma \rho_i = \Sigma \frac{m}{e^2 n \tau_i} = \frac{m}{e^2 n} \frac{G}{\tau_0} \quad (5)$$

as in Matthiessen’s rule (e.g. Eq.(16.22) of Ashcroft and Mermin[1]; of course ‘without impurity’). Here ρ_i is defined as $\rho_i = m / (e^2 n \tau_i)$, and use is made of $\Sigma (1/\tau_i) = (\Sigma_{i=1}^G 1) / \tau_0 = G / \tau_0$. In order to obtain an equality between Eq.(5) and Eq.(2) which uses n_{atom} , $n = n_{\text{atom}}$ is required as in Eq.(4). Thus, although the assumption that every band takes the same τ_0 might seem a very crude assumption, we should remember that G -values were guessed by assuming that every band has equally ‘one’ contribution each to G with the same τ_0 , resulting in good agreement with observations.

As an alternative option, if we assume $\sigma = \Sigma \sigma_i = \frac{e^2 n \tau_0}{m} \times G$, as in Eq.(13.24) of Ashcroft and Mermin[1] again with $\tau_i = \tau_0$ for all i , we obtain

$$\sigma = \Sigma_i \sigma_i = \frac{e^2 n_{\text{atom}} \tau_0}{m} \times G Z_\sigma = \sigma_{\text{Eq.(2)}} \times G^2 Z_\sigma. \quad (6)$$

This is compatible with Eq.(2) only when $Z_\sigma = 1$ and $G = 1$ since $G \geq 1$ and $Z_\sigma \geq 1$. Hence we discard this latter option.

Note that only Ashcroft and Mermin[1] in p.250 mention, without any theoretical explanation, on the additive current density and hence $\sigma = \Sigma_i \sigma_i$, but all the other text books cited in this paper and some other books did not say anything on this important issue. On the other hand, the Matthiessen rule is mentioned in many books, expressing that it is applicable if two (or more) distinguishable sources of scattering as in $\rho = \Sigma_i \rho_i$, but it is nowhere mentioned that ‘distinguishable sources’ should not include different electron bands. Thus in this empirical paper we adopted Eq.(5), which is consistent to observations, though Z -values are not needed in Eqs.(1-2) (see theoretical derivation of Eq.(11) supporting $Z \approx 1$).

We look these results of Eqs.(4) and (5) from the macroscopic stand point of view. The classical equation of motion for a one electron is $m dV_x / dt = -e E_x - m V_{\text{drift}} \nu$, where E_x is the imposed electric field and V_{drift} is the effective drift velocity both in x -direction and ν is the number of collisions in unit time. Then the option we adopt means that the total resistive force for one electron $-m V_{\text{drift}} \nu$ is the summed resistive force of each band in elemental metals, which we consider as mutually independent. Namely as Eq.(2) or (5), the sum of each band means $\nu = \sum \nu_i = \sum (1/\tau_i) = G / \tau_0$ and $Z_\sigma = 1$, e.g. either for $G = 3$ in $\text{In}^{49}(5s^25p^1)$ or $G = 4$ in $\text{Pb}^{82}(6s^26d^2)$ with the same τ_0 . Also even if one doubts (10- x)-rule or

1/2-rule, the result for G without these rules is not worse than a factor of about 2 for those metals which employed either one of the two rules.

The conclusion of this section is simply $Z_\sigma = 1$ or $n = n_{\text{atom}}$, namely Eq.(4). This means that the number of electrons per one atom is effectively only one, which is responsible for σ when given the electric fields and λ when given the temperature gradient, but $Z_\sigma = 1$ does not necessarily apply for other physical quantities such as cohesive energy or with imposed magnetic fields. Further, $Z_\sigma = 1$ is mutually consistent with the condition that every $\nu_i \equiv 1/\tau_i$ is the same as $1/\tau_0$. The total collision frequency is $\nu_{\text{tot}} = \sum_{i=1}^G \nu_i = G/\tau_0$. Here ν_{tot} acts in the resistive force for ‘a single electron’ in the classical equation of motion as $-mV_{\text{drift}}\nu_{\text{tot}} = -mV_{\text{drift}}G/\tau_0$.

5. Effective Mass \simeq True Electron Mass for σ

This section inspects if the use of the true electron mass m in Eq.(2) is allowed rather than the effective electron mass m^* , even though Eq.(2) satisfies observations quite well. For this purpose we use electron specific heat at constant volume C_{Ve} , which is only ‘discernible’ below a few Kelvin (of course C_{Ve} is not zero even at high temperature). The ratio of the observed $C_{\text{Ve-obs}}$ to

$$C_{\text{Ve-free}} = \frac{\pi^2}{3} D(E_{\text{F}})_{\text{free}} k_{\text{B}}^2 T = \frac{\pi^2}{2} \frac{k_{\text{B}}^2 T}{E_{\text{F}}} \quad (7)$$

from the free electron model is conventionally expressed as m^*/m (m^* is called the thermal effective electron mass [3]). Here $D(E_{\text{F}})_{\text{free}} = 3/2E_{\text{F}}$ is the density of states/atom for the free electron model. This comes from $C_{\text{Ve-free}} \propto E_{\text{F}}^{-1} \propto m$ and similarly we designate m^* from $C_{\text{Ve-obs}} \propto m^*$. The ratio $m^*/m = C_{\text{Ve-obs}}/C_{\text{Ve-free}}$ amounts to ten or more for the transition metals [1–3].

Extensive numerical calculations by Moruzzi et al.[16] for non-free electron models (the local density theory and the ‘muffin-tin’ model) tabulate, besides the calculated Fermi energy, the density of states $D(E_{\text{F}})$ at the Fermi energy for each metal. Using the latter expressed as $D(E_{\text{F}})_{\text{Morz}}$, we find

$$\frac{m^*}{m} = \frac{C_{\text{Ve-obs}}}{C_{\text{Ve-theory}}} = \frac{C_{\text{Ve-obs}}}{\pi^2 D(E_{\text{F}})_{\text{Morz}} k_{\text{B}}^2 T/3} = 1.05 \pm 0.29 \quad (8)$$

for 24 metals ($C_{\text{Ve-obs}}$ from Kittel[3]). Below shows some indication of the accuracy of m^*/m in the theory[16], other than the observational errors. Six metals not included in the above 24 metals show $m^*/m > 2.0$, where the values of m^*/m are 4.9(Sr), 3.1(Y), 2.6(Sc), 2.5(Mn), 2.4(V), and Nb(2.4). For example, $D(E)$ plotted against E for Sr shows that E_{F} is in the bottom of a sharp valley [16] suggesting that $D(E_{\text{F}}) = 0.31 \text{ states/eV}\cdot\text{atom}$ could have been larger, and accordingly m^*/m may become closer to unity, if the theory becomes further refined (cf. $D(E_{\text{F}})=0.45$ in simpler sodium). A similar situation is seen in Y [$D(E_{\text{F}})=1.41$], which has a steep peak of $D(E)$ just below E_{F} .

Taking into account of errors from theory and observation, this result of $m^* \approx m$ supports to use the true electron mass m in Eq.(2) (no magnetic fields), besides Eqs.(1) and (2) reproduce the observations quite well. Note that the departure from unity of $\sigma/\sigma_{\text{obs}}$ in Fig.1 (b)-upper does not seem to be correlated with m^*/m , nor with the lattice structures such as fcc or bcc.

The following will clarify that m^*/m from C_{Ve} should be the same as m^*/m to be used in σ at room temperature range. If one adopts the classical thermal conductivity $\lambda_{\text{classical}} = \frac{1}{3} C_{\text{V}} L_{\text{mfp}} V \times n$, we recover Eq.(2) for λ multiplied by G , inserting $C_{\text{V}} = C_{\text{Ve-free}} = (\pi k_{\text{B}})^2 T / (2E_{\text{F}}) = (\pi k_{\text{B}})^2 T / (m V_{\text{F}}^2)$, $L_{\text{mfp}} V = V_{\text{F}}^2 \tau_0$, and $n = n_{\text{atom}}$ from Eq.(4) (L_{mfp} is the mean free path). The classical form $\lambda_{\text{classical}}$ is now considered to be applicable to a single band, $G = 1$, or rather if we change the definition from $\lambda_{\text{classical}}$ to $\lambda_{\text{semi-classical}} = \frac{1}{3} C_{\text{V}} L_{\text{mfp}} V n / G$, then we recover exactly Eq.(2) for λ . Since $\lambda_{\text{semi-classical}} \propto C_{\text{Ve}} \propto E_{\text{F}}^{-1} \propto m^*$, this shows that use of $m^*/m \approx 1$ is supported also in λ , which in turn should use the same electron mass in σ of Eq.(2).

The conclusion of this section is the same as the section title, though one might add ‘which is found using $C_{\text{Ve-obs}}/C_{\text{Ve-theory}}$ ’.

6. Reducing Bardeen’s τ to τ_0

This section will relate our $\tau_0 = \hbar/k_{\text{B}}T$ to the collision time of Bardeen[7] τ_{B} used for $\sigma = e^2 n \tau_{\text{B}} / m$ in his Eq.(6)≡Eq.(bd6), which is applicable to the monovalent metals at T_{room} range. Eq.(bd52) is

$$1/\tau_{\text{B}} = \hbar \pi^3 n k_{\text{m}}^{-2} (dk/dE)_{\text{m}} (T/M k_{\text{B}} \Theta^2) C^2. \quad (9)$$

This (\hbar^2 should read \hbar as above) is converted to

$$\frac{\tau_{\text{B}}}{\tau_0} = \frac{3M}{\pi m} \left(\frac{k_{\text{B}} \Theta}{C} \right)^2 = \frac{4}{2^{1/3} \pi} \frac{3M C_{\text{s}}^2 E_{\text{F}}^2}{E_{\text{F}} C^2} = 1.01 \left(\frac{C}{E_{\text{F}}} \right)^{-2}. \quad (10)$$

The first equality used $k_{\text{m}}(dE/dk)_{\text{m}} = 2E_{\text{F}} = \hbar^2 k_{\text{m}}^2 / m$ with $n = k_{\text{m}}^3 / 3\pi^2$. The subscript m refers to maximum values. This first equality is equivalent to Eq.(12.3) of $1/\tau$ in Jones’s review[20]. The second equality uses $k_{\text{B}} \Theta = C_{\text{s}} \hbar q_{\text{m}} = 2^{1/3} C_{\text{s}} \hbar k_{\text{m}}$ [Eq.(bd11)], where C_{s} is the sound speed, $q_{\text{m}} = 2^{1/3} k_{\text{m}}$ is from $n = n_{\text{atom}} = q_{\text{m}}^3 / 6\pi^2$, and C is the distorted potential (interaction constant of Sommerfeld and Bethe[21]). The final equality adopts the relation (see below)

$$3M C_{\text{s}}^2 \approx E_{\text{F}}, \quad (11)$$

for atom of mass M . Then if $(C/E_{\text{F}})^2 = 1$ for all monovalent metals, we obtain $\tau_{\text{B}} \approx \hbar/k_{\text{B}}T \equiv \tau_0$. Bardeen[7](p.697) may “have underestimated the Umklapp processes so that true values of C/E_{F} should be larger by perhaps ten or fifteen percent” than the average value of 0.8 of his theory for 7 monovalent metals. Namely he implies $\tau_{\text{B}}/\tau_0 = 1.2 \sim 1.3$, while for the same

metals (Fig.1b-upper) $\tau_{\text{obs}}/\tau_0 = \sigma_{\text{obs}}/\sigma = 1.1 \pm 0.2$. [See also the original defining Eq.(34.24) of C as “the mean kinetic energy of conducting electrons” in Sommerfeld and Bethe[21], their Eq.(34.31) above, and Sect. 36 c) p.191.]

We empirically find below that Eq.(11) holds if we assume $C_s^2 = C_{\text{tot}}^2$, where $C_{\text{tot}}^{-3} \equiv C_{\text{long}}^{-3} + 2C_{\text{trans}}^{-3}$ as in Eq.(5.18) of Ibach and Lüth[2] for the total of longitudinal and transverse waves. Namely $3MC_{\text{tot}}^2/E_F^{\text{Morz}} = 0.93 \pm 0.20$ is obtained for 13 metals of Be, Mg, Al, Cr, Fe, Ni, Cu, Zn, Pd, Ag, and Cd, and further Ti and Zr (all metals with tabulated C_{long} and C_{trans} values[22]) by use of the theoretical E_F^{Morz} by Moruzzi et. al[16], while if one uses E_F^{free} we find $3MC_{\text{tot}}^2/E_F^{\text{free}} = 1.22$. Similar values are obtained from Papaconstantopoulos[23], where the calculated Fermi energy is still somewhat different from Moruzzi et al.[16] even in Na; namely $E_F/E_F^{\text{free}} = 0.90$ in the former and 1.07 in the latter. [There seems no numerical correlation between $3MC_{\text{tot}}^2/E_F^{\text{Morz}}$ and $\sigma/\sigma_{\text{obs}}$, which might have related to e.g. deformation potentials $\propto C/E_F$.]

Likewise if we use the tabulated slender ‘rod’ sound speeds [22], we find $MC_{\text{rod}}^2/E_F = 1.26 \pm 0.24$ using theoretical E_F for 11 metals without Ti and Zr (no C_{rod} data), while $MC_{\text{rod}}^2/E_F^{\text{free}} = 1.78$. This may be a one dimensional version of Eq.(11). Since Eq.(11) is independent whether external electric fields exist or not, C_{tot} seems more appropriate than C_{rod} .

Theoretically Eq.(11) can ‘roughly’ be derived as follows. We convert $C_{\text{tot}}^2 = \omega^2/k^2$ by using $\omega^2 = \Omega_i^2/\epsilon = \Omega_i^2 k^2/(k^2 + k_0^2)$ and ion plasma frequency $\Omega_i^2 = 4\pi e^2 nZ/M$. Here $\epsilon(k)$ is the dielectric constant and k_0 is the Thomas-Fermi wave number defined by $k_0^2 = 4\pi e^2 \partial n/\partial \mu$ (μ =chemical potential $\approx E_F$). If one uses the state density at the Fermi energy for the free electron model, $\partial n/\partial \mu = 3n/2E_F$, the Bohm-Staver relation $3MC_{\text{tot}}^2 = 2ZE_F k_0^2/(k^2 + k_0^2) = 2ZE_F$ is obtained for $k \rightarrow 0$ [e.g. Eqs.(26.2-8) of Ashcroft and Mermin[1]]. This holds even if we replace $M\Omega_i^2$ by $M\Omega_i^2 - k^2 V'$ from the ‘shallow’ constant potential $V'(k)$ in the ion core (see e.g. Eq.(6.92) and Fig.88(c) of the screened pseudo-potential in Ziman[24]). Incidentally Ziman notes that the formula for the screened potential, i.e. his Eq.(6.93)=[(6.92)/ $\epsilon(k)$] “is the formula derived by Bardeen in 1937 for the matrix elements of the electron-phonon interaction...”. On the other hand if $k \rightarrow k_0$ and $Z=1$ are assumed, we recover exactly Eq.(11), which is also valid if the core potential part is negligible such as in the often-used-Ashcroft model of $V' = 0$ [25]. (The Thomas-Fermi screening is the spherically symmetric Fourier transform of the screened electron potential $\phi(r) = -Ze^2 \exp(-k_0 r)/4\pi\epsilon_0 r$.) Equation(11) implies that ion vibrations can be expressed by the electron properties or motions in (nearly) thermal equilibrium.

The conclusion of this section is that Bardeen’s τ_B is found to be equal to $\tau_0 = \hbar/k_B T$ of Eq.(1) within 10 to 20% accuracy using primarily the empirical relation Eq.(11). Conversely if one adopts the Bardeen theory,

Eq.(1) is theoretically derived with $G = 1$ in Eq.(2) within the same accuracy. As for the absolute values of the electrical resistivity in the non-monovalent metals, G -values, i.e. the number of responsible electron bands take care also at T_{room} range.

7. Collision Time of Eq.(1) from Much Reduced Effective Electron Density

The very fact that the Bardeen τ_B can, in the end, be expressed without any parameters related to ions as shown in Sect.6 leads to a conjecture that the theory might be constructed without ‘formally’ introducing phonons, which is treated in this and the following sections. For $T \ll T_{\text{room}}$ we briefly discuss in Sect.9.

As is well-known $L_{\text{mfp}} = V_F \tau$ becomes 40nm in Cu for example, if one uses τ from the observed electrical resistivity, or from Eq.(1) giving 2.55×10^{-14} s at 300K. This L_{mfp} is very much larger than the mean atomic distance of $d \equiv n_{\text{atom}}^{-1/3} = n^{-1/3}$, e.g. $d(\text{Cu}) = 0.23\text{nm}$. This does not mean that the collision cross-section S is many order of magnitudes smaller than $d^2 = (0.23\text{nm})^2$. (If we adopt the observationally supported Eq.(1), $S \simeq d^2/2$ is derived as shown below.) But in fact only a small fraction of $\alpha k_B T/E_F$ is able to collide elastically because the Fermi distribution function is saturated at unity below E_F ($\alpha \approx 3$ or so, see below; $k_B T/E_F = 3.7 \times 10^{-3}$ for Cu).

We then adopt the following simple form

$$1/\tau = n_{\text{eff}} V_F S, \quad (12)$$

with the defining equations of

$$n_{\text{eff}} = \frac{\alpha k_B T}{E_F} n \quad S = \alpha_s d^2. \quad (13)$$

Here $S[\text{m}^2]$ is the ionic cross-section with a parameter α_s for an assumed square shape area d^2 . We stress that the form of Eqs.(12-13) is expected already in Eq.(9) from Bardeen because $1/\tau_B \propto n k_m^{-2} T \propto n S T$. Using the constant electron speed of V_F , Eq.(12) immediately yields

$$\tau = \frac{E_F}{\alpha k_B T} \frac{1}{n V_F S} = \frac{1}{\alpha k_B T} \frac{\hbar k_F}{2} \frac{(3\pi^2)^{1/3}}{\alpha_s k_F} = \frac{3.09}{2\alpha\alpha_s} \frac{\hbar}{k_B T}, \quad (14)$$

where the second equality used $E_F/V_F = \hbar k_F/2$ and $1/nS = (3\pi^2)^{1/3}/\alpha_s k_F$ from $n = k_F^3/3\pi^2$ and $d = n^{-1/3}$.

We estimate α and α_s below. Regarding α , though it is often stated $\alpha = 3 \sim 4$ from the rough inspection of the steeply decreasing part of the Fermi-distribution as compared with the almost constant part, we wish to be more specific about α . The electron specific heat given by $C_{\text{Ve-free}} = \frac{\pi^2}{2} k_B^2 T/E_F$ of Eq.(7) for the free electron model, which may be applicable to alkali and noble metals, can be rewritten as

$$C_{\text{Ve-free}} = \frac{3k_B}{2} \frac{\alpha k_B T}{E_F} = C_{\text{Ve-all}} \frac{n_{\text{eff}}}{n} \quad \alpha = \pi^2/3. \quad (15)$$

This relation is usually interpreted as equal to $C_{\text{ve-all}}=3k_B/2$ for all electrons (freedom of 3 in unit energy $k_B T/2$, in contrast to freedom of 6 in lattice) multiplied by a fraction of the responsible electron number density due to the Fermi distribution. Therefore we adopt this $\alpha = \pi^2/3 \simeq 3.3$. The origin[1, 3] of the value $\pi^2/3$ is as follows: $\pi^2/3 = \int_{-\infty}^{\infty} x^2(1-f)fdx$, where f is the Fermi distribution function for the energy ϵ , $f = 1/(\exp(x) + 1)$, $x = (\epsilon - E_F)/k_B T$ and $-df/dx = (1-f)f$ (very close to a Gaussian). Since $\int_{-\infty}^{\infty} (1-f)fdx = 1$, we can regard this α as equal to the second (lowest non-zero) moment of $(1-f)f$, $\langle x^2 \rangle_{(1-f)f} = \pi^2/3 = \alpha$, or the spread of $(1-f)f$ in unit of $k_B T$, hence α has a clear physical meaning.

We turn to the estimation of the upper and lower limit of the cross-section S , i.e. α_s . The upper limit is $S \leq d^2 = n^{-2/3}$, namely $\alpha_s = 1$, because in this expression the space around any ion core is filled up, and no electrons can freely pass. This is true for any of the 3-D Bravais lattice structures, or for different forms of S such as $S_{\text{max}} = d^2 \equiv \pi r_d^2$. The lower limit is somewhat indeterminate, but we take a rather safer Bohr value of $S_{\text{min}} = \pi r_0^2$. The cross section $S_{\text{Eq.(1)}}$ expected from Eq.(1) gives is in fact $S_{\text{Eq.(1)}} = 0.47d^2 \approx d^2/2$ (or $\alpha_s \approx 1/2$), where use is made of Eq.(14) and $\alpha = 3.3$ in Eq.(15).

Thus we reach

$$\pi r_0^2 \leq S_{\text{Eq.(1)}} \approx d^2/2 < d^2. \quad (16)$$

Here e.g. in Cu, $\pi r_0^2 = 0.170d^2$ and $d^2/2 = 2.94\pi a_0^2$. Therefore without using Eq.(1), expected cross sections fall rather narrow ranges of $0.17d^2 < S < d^2$ (Cu) and it may well be so for the majority of elemental metals at T_{room} -range as long as $m^* \approx m$ and $Z_\sigma \approx 1$ hold as shown in Sects.4 and 5. The method of this section at the ‘present form without further elaboration’ cannot be more accurate than this, though the simplicity may count.

We call attention again to the fact that any concept of phonon or lattice vibration were not needed in the above. In fact, in the expression of $\tau \propto \hbar/k_B T$ in Eq.(14), ‘ \hbar ’ arises from ‘ $E_F/V_F' \propto \hbar$ ’ concerning electrons, and ‘ $k_B T$ ’ is from $n_{\text{eff}} \propto T$, which originally came from the steeply decreasing part of the ‘electron’ Fermi distribution.

In many textbooks, it is argued that the only cause of the non-zero resistivity stems from the ion vibration (at the room temperature range). But since the ‘ion’ vibration can be expressed by Eq.(11) in terms of the (‘electron’) Fermi energy, we may as well express the electrical conductivity in terms of electron behavior.

Thus conversely, once the cross-section of order of $S \approx d^2/2$ is accepted, we can conclude that τ_0 is on the order of $\hbar/k_B T$, and that the precise value is supported as $\tau_0 = \hbar/k_B T$ from the observations as in Sect.2 for elementary metals at T_{room} . Since the electron half-wavelength at the Fermi energy is $\lambda_F/2 = \pi/k_F = (\pi/3)^{1/3} n^{-1/3} = 1.016d$, $S = (\lambda_F/2)^2/2$ may be used as an alternative expression for S .

We close this section by inspecting how to interpret n_{eff}/n in terms of the Bardeen theory. If E_F which used E_F^{free} above is different from the true E_F , we must multiply $E_F/E_F^{\text{free}} \times 2/(d\log E/d\log k)_m$. Ignoring this factor and $(C/E_F)^2$, we find that Eq.(9) is physically equivalent to Eq.(12). Bardeen’s Eq.(bd7), from which Eq.(bd52)=Eq.(9) is obtained, is

$$\frac{1}{\tau_B} = \frac{k_m^2}{\pi \hbar (dE/dk)_m} \int_0^\pi |M_{kk'}|^2 (1 - \cos \theta) \sin \theta d\theta, \quad (17)$$

where $|M_{kk'}|$ is the transition matrix for $\mathbf{k} \rightarrow \mathbf{k}'$ [$\cos \theta = (\mathbf{k} \cdot \mathbf{k}')/kk'$ and \mathbf{k} is the vector parallel to the applied electric field]. In order to see the magnitude of $|M_{kk'}|^2$, we first convert the factor before the integration in Eq.(17) to $km/\pi \hbar^3 = 3\pi n/2\hbar E_F$. Then we obtain, assuming that $\tau_B = \hbar/k_B T$ holds exactly,

$$\langle |M_{kk'}|^2 \rangle_\theta \equiv \int_0^\pi |M_{kk'}|^2 (1 - \cos \theta) \sin \theta d\theta = \frac{2E_F k_B T}{3\pi n}. \quad (18)$$

If $|M_{kk'}|$ vanishes below $\theta < \pi$, the upper integration limit can be $\theta < \pi$. See below a different normalization form at the section end.

Conventionally $M_{kk'}$ is expressed by a product of the structure factor S_t and the form factor $m_{kk'}$, namely $M_{kk'} = S_t m_{kk'}$. Here $|S_t|^2 = |q|^2 |a_q|^2 = \frac{3}{2} k_B T/E_F$, where the first equality is from Rossiter’s[25] Eqs.(5.9b) and (A19) ($|u_q| \equiv |a_q|$ is the vibration amplitude) and the second is from $|a|^2 = k_B T/2Mq^2 C_s^2$ of Eqs.(bd9-10) and present Eq.(11). To be consistent with Eq.(18), we need to adopt $\langle |m_{kk'}|^2 \rangle_\theta = (\frac{2}{3} E_F)^2/\pi n$. Thus we can express n_{eff}/n in terms of $\langle |M_{kk'}|^2 \rangle_\theta$ or $|S_t|^2$ as

$$\frac{n_{\text{eff}}}{n} \equiv \alpha \frac{k_B T}{E_F} = \alpha \frac{3\pi n \langle |M_{kk'}|^2 \rangle_\theta}{E_F^2} \approx 2|S_t|^2. \quad (19)$$

Similarly the amplitudes of ion vibration is $|a_q|/(d/2) = 0.63(k_B T/E_F)^{1/2}$, again only as functions of T and E_F [note that $a_q/(d/2) = 0.04$ at 300K in Cu]. By an appropriate normalization to the wave function, using azimuth angle ϕ and $\int_0^{2\pi} d\phi / \int_0^\pi (1 - \cos \theta) \sin \theta d\theta = \pi$, Eq.(18) changes to $2E_F k_B T/3$, and $\langle |m_{kk'}|^2 \rangle_\theta$ changes to $(\frac{2}{3} E_F)^2$; in the latter in modern treatments, $m_{kk'} \approx -\frac{2}{3} E_F$ for $q/2k_F = \sin(\theta/2) = 0$, while $m_{kk'} \approx 0$ at $q/2k_F \approx 1$ as shown e.g. in Fig.(5.30) or Figs.(6.5-6) of Rossiter[25].

8. Fluctuation Dissipation Theorem in Interpreting the collision time, Eq.(1)

Now, examples of the ratio of τ_0 from Eq.(2) to τ_{obs} determined from Eq.(1) using the experimental resistivity and $G = 1$ are $\tau_0/\tau_{\text{obs}} = 0.88(\text{Na})$, $0.98(\text{Rb})$, $1.05(\text{Cu})$, and $0.95(\text{Au})$ at room temperature ranges, T_{room} . Because of this remarkable closeness to unity, it is tempting to assume that there may be an extremely simple explanation for $\tau_0 = \hbar/k_B T$, which is presented in this section,

using monovalent metals, since multivalent metals can be treated by Eq.(2) with the guessed G -values and $Z_\sigma = 1$.

For this purpose, first we search for the connection of τ_0 to the fluctuation dissipation theorem, FDT[26–28]. The classical representation of FDT for the isotropic electrical conductivity σ is as Eq.(9.1) in the seminal paper of Kubo [10]

$$\sigma = \frac{ne^2}{k_B T} \int_0^\infty \langle v_x(0)v_x(t) \rangle dt. \quad (20)$$

Here $v_x(t)$ is the fluctuating electron velocities parallel to the given electric field E_x , and an obvious relation holds for the autocorrelation $\langle v_x(0)v_x(t) \rangle = \langle v_x(t_1)v_x(t_1+t) \rangle$ for any t_1 in the assumed stationary stochastic processes. We assume that the time average of any physical quantity $\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(t)dt$ is equal to ensemble average \bar{A} (ergodic).

The thermal fluctuation is of course expected without giving external electric fields, and is on the order of $(4f(1-f)/N)^{1/2}$, where $f(E)$ is the Fermi distribution function and N is the total number of electrons in a volume V [29]. Thus the fluctuation is occurring around the Fermi energy E_F with the width $\approx 3k_B T$. Historically the macroscopic counter part originates from the 1928-Nyquist ‘fluctuation’ theorem.

We split Eq.(20) in two parts by introducing the true electron mass m .

$$\sigma = ne^2 \tau_{\text{cor}} / m, \quad (21)$$

where

$$\tau_{\text{cor}} \equiv \frac{m}{k_B T} \int_0^\infty \langle v_x(0)v_x(t) \rangle dt. \quad (22)$$

Thus in order to obtain $\tau_{\text{cor}} = \tau_0 \equiv \hbar/k_B T$, we ‘need’ (but not yet we ‘obtain’)

$$H \equiv \frac{\tau_{\text{cor}} k_B T}{2} = \int_0^\infty \langle \frac{1}{2} m v_x(0)v_x(t) \rangle dt = \frac{\hbar}{2}. \quad (23)$$

We then adopt $H = \langle \frac{1}{2} m v_x^2 \rangle \langle \Delta t \rangle$, where $\langle \Delta t \rangle$ is chosen to reproduce the value of H as the average of the time span of this integration. This is reasonable if we consider that the autocorrelation function rapidly decreases as $\exp(-t/\tau)$ for relaxation processes [or in the (first) Markov processes]. We interpret Eq. (23) as expressing

$$H = \langle \frac{1}{2} m v_x^2 \rangle \langle \Delta t \rangle \equiv \langle (\Delta E)_{\text{kin-x}} \rangle \langle \Delta t \rangle = \frac{\hbar}{2}. \quad (24)$$

Here $\langle \frac{1}{2} m v_x^2 \rangle \equiv \langle (\Delta E)_{\text{kin-x}} \rangle$ literally means the fluctuating kinetic energy of electrons in the x direction. If $(\Delta E)_{\text{kin-x}} \Delta t = \Delta(p_x^2/2m) \Delta t = (p_x/m) \Delta p_x \Delta t = \Delta p_x v_x \Delta t = \Delta p_x \Delta x$ is used, as in e.g. Sect.10 of Messiah[30], we still obtain, dropping $\langle \dots \rangle$ for simplicity,

$$H = (\Delta E)_{\text{kin-x}} \Delta t = \Delta p_x \Delta x = \frac{\hbar}{2}. \quad (25)$$

Conversely, assume that $H = \langle \frac{1}{2} m v_x^2 \rangle \langle \Delta t \rangle$ takes the minimum uncertainty value of $\hbar/2$ as suggested in Eq. (24) or Eq.(25), then Eq.(23) immediately leads to $\tau_{\text{cor}} = \hbar/k_B T = \tau_0$. It seems rather difficult to escape from this statement.

We remark below some relations among Eqs.(20)-(25). If we assume Eqs.(21) and (22), we obtain Eq.(20), which may be regarded as a simplest derivation of the fluctuation-dissipation theorem in the classical form if so wished. [In this logic Eq.(21) with an unspecified τ can be obtained from the Boltzmann equation (Appendix), and we regard that this τ is specified (or defined) by Eq.(22).] Or else from Eqs.(20) and (22), we obtain Eq.(21), the Drude form with $\tau = \tau_{\text{cor}}$! Further, if we assume

$$\langle \Delta t \rangle = \tau_{\text{cor}} \quad (26)$$

and use $\tau_{\text{cor}} = m < v_x^2 \rangle \langle \Delta t \rangle / k_B T$ from Eq.(23) and Eq.(24), we find one dimensional equipartition

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T, \quad (27)$$

which is quite reasonable, in view of the fact that the fluctuation is occurring around E_F . In fact derivation of the classical Nyquist theorem for macroscopic electric circuits uses this equipartition at T_{room} range. In the above $\langle \frac{1}{2} m v_x^2 \rangle$ which is non-negative comes actually from $(\Delta E)_{\text{rms}} \equiv \langle (E_{\text{kin-x}} - \frac{1}{3} E_F)^2 \rangle^{1/2} \equiv \langle (\Delta E_{\text{kin-x}})^2 \rangle^{1/2} = \frac{1}{2} m \langle v_x^2 \rangle$. Thus we obtain $(\Delta E)_{\text{rms}} = k_B T/2$. For a metal in a heat bath, since the temperature entering $\tau_0 = \hbar/k_B T$ is by itself a fluctuating quantity expressed as $\langle (\Delta T)^2 \rangle^{1/2} / T = (k_B / C_{V-\text{lattice}})^{1/2} = 1/(3N)^{1/2}$ (Landau and Lifshitz[29], Chap.12, Eq.(112.6); N is the total number of ions in a Volume V), Δt may be expressed as $\langle \tau^2 \rangle^{1/2} = \langle (\Delta t)^2 \rangle^{1/2} \equiv (\Delta t)_{\text{rms}}$.

Now, our task is to understand why the empirically supported $\frac{1}{2} \int_0^\infty \langle m v(0)v(t) \rangle dt \equiv \langle \frac{1}{2} m v^2 \rangle \langle \Delta t \rangle = \frac{\hbar}{2}$ holds; namely Eq.(24) or Eq.(25). Our proposal is as follows. Consider one electron heading toward x direction with the speed of $V_F = (2E_F/m)^{1/2}$, then it effectively collides with an ion until it passes e.g. $180 \times$ lattice-distance in Cu at 300K ($L_{\text{mfp}}/d = V_F \tau_0 / n^{-1/3} = \frac{2}{3} \frac{E_F}{k_B T}$; $L_{\text{mfp}} = V_F \tau_0$ is the mean free pass). Namely electrons are nearly free. The elementary quantum physics teaches that the wave function of a free electron is expressed as

$$\Psi(x) = \frac{1}{a^{1/2} \pi^{1/4}} \exp \left(-\frac{(x-x_0)^2}{2a} + \frac{ip_0 x}{\hbar} \right). \quad (28)$$

This, in the words of Leighton[31] p.105, exhibits the minimum uncertainty product $\Delta x \Delta p = \hbar/2$, hence Eq.(25) holds. Eq.(28) is regarded to the classical statement that a one-dimensional particle is located at coordinate x_0 and is moving with momentum p_0 . Further detail[31] is in p.98; $(\Delta x)^2 = a^2/2$, $(\Delta p)^2 = \hbar^2/2a^2$, $\langle x \rangle = x_0$, $\langle p \rangle = p_0$, $\phi(p) = \frac{1}{\pi^{1/4}} \left(\frac{a}{\hbar} \right)^{1/2} \exp[-(p-p_0)^2 a^2/2\hbar^2] \exp[-i(p-p_0)x_0/\hbar]$, where $\phi(p)$ is the wave function for momentum.

The above result is strengthened by using the Bloch form of the wave function Ψ in the time independent Schrödinger equation $H\Psi = (-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}))\Psi = E\Psi$, where $U(\mathbf{r}) = U(\mathbf{r} + \mathbf{b})$ is the potential energy within one-electron approximation.

$$\Psi = u(\mathbf{r})\exp(i\zeta) = u(\mathbf{r} + \mathbf{b})\exp(i\zeta) \quad (29)$$

Here $|\mathbf{b}|$ is the lattice distance of order of d and $\zeta \equiv \mathbf{k} \cdot \mathbf{r} = \mathbf{p}/\hbar \cdot \mathbf{r}$; that is the plane wave, i.e. free electrons, modified by the periodic lattice potential. The average of Ψ becomes

$$\langle \Psi \rangle = \langle u \rangle \langle \exp(i\zeta) \rangle \approx \langle u \rangle \exp(-\frac{\langle \zeta^2 \rangle}{2}) \quad (30)$$

for a real variable of ζ , where $|\zeta| < 1$ and $\exp(-i\zeta) = \exp(i\zeta)$, i.e. even probability (see e.g. Appendix C of Rossiter[25], though a misprint corrected below; see also Eqs.(2.105-107) of Ziman[8] on Debye-Waller factor, which seems valid without the condition $|\zeta| < 1$). Here an approximation in Eq.(30) comes from

$$\langle \exp(i\zeta) \rangle = \langle 1 + i\zeta - \frac{\zeta^2}{2} - i\frac{\zeta^3}{6} + \frac{\zeta^4}{24} - \dots \rangle \quad (31)$$

$$= 1 - \frac{\langle \zeta^2 \rangle}{2} + \frac{\langle \zeta^4 \rangle}{24} - \dots \quad (\text{even function}) \quad (32)$$

and

$$\exp(-\frac{\langle \zeta^2 \rangle}{2}) = 1 - \frac{\langle \zeta^2 \rangle}{2} + \frac{\langle \zeta^4 \rangle}{8} - \dots, \quad (33)$$

where accuracy is $\sim 3\%$ for $\zeta = 0.8$ or 0.5% for $\zeta = 0.5$, using $\frac{\zeta^4}{8} - \frac{\zeta^4}{24} = \frac{\zeta^4}{12}$.

This means that the wave function takes the minimum wave function say in x direction, where the wavelength $\lambda = 2\pi/k$ should be large enough so that $\lambda \gg d$ (d =the mean atomic distance) requires $\zeta = kx \ll x/d < 1$ to satisfy the approximation imposed above. Thus the allowed extension of the present minimum wave function should be $x < d$, though the condition of $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{b})$ in Eq.(29) allows us that it can be enormously extended. To recall the derivation in a most elemental way, we adopt

$$\phi(x) = (a/\pi)^{1/4} e^{-ax^2/2}, \quad (34)$$

where $\int |\phi(x)|^2 dx = 1$ and $a > 0$. We obtain

$$\langle (x - \langle x \rangle)^2 \rangle \equiv \langle (\Delta x)^2 \rangle = \int x^2 |\phi(x)|^2 dx = \frac{1}{2a}, \quad (35)$$

using $\langle x \rangle = 0$. The corresponding wave function for p which is the Fourier transform of $\phi(x)$ is calculated to be $\psi(p) = \int_{-\infty}^{\infty} \phi(x) \exp(ixp/\hbar) dx = e^{-p^2/2a\hbar^2} / (\pi a \hbar)^{1/4}$. We similarly obtain

$$\langle (\Delta p)^2 \rangle = \frac{a\hbar^2}{2}. \quad (36)$$

Hence $\langle (\Delta x)^2 \rangle^{1/2} < \langle (\Delta p)^2 \rangle^{1/2} = \frac{\hbar}{2}$ is derived from Eqs.(35-36). [In the pure classical wave of $\psi(k) =$

$\int \phi(x) \exp(ikx) dx$, we naturally obtain $\langle (\Delta x)^2 \rangle^{1/2} < \langle (\Delta k)^2 \rangle^{1/2} = \frac{1}{2}$, without \hbar .] The above derivations of $\tau_0 = \hbar/k_B T$ do not use the ion vibration, since Eq.(20) is independent of it, namely only the electron motions, though Eq.(11) acts for this connection.

The conclusion of this section is that if nearly free electrons are assumed, $\Delta x \Delta p_x = \hbar/2$ is satisfied. This means that Eq.(25) or Eq.(24) should be satisfied. In turn, Eq.(23) from the fluctuation dissipation theorem should hold. Thus we obtain Eq.(1), assuming $\tau_{\text{cor}} = \tau_0$.

9. Discussion

We remark on the observed temperature dependence of the electrical resistivity $\rho = 1/\sigma$. If we plot ρ/T as a function of Θ , where Θ is the Debye temperature, then we find that $\rho/T = \text{constant}$ applies only in the following small range:

$$T \leq 0.5T_{\text{melt}} \quad (37)$$

$$0.5 \leq T/\Theta \leq 2 \quad (38)$$

Here T_{melt} is the melting point. Surprisingly, T beyond $\sim 0.5T_{\text{melt}}$, suddenly ρ changes to behave as $\rho \propto T^{-2}$ so that the upper end of 2 in Eq.(38) results, though dependent upon various 19 metals plotted (see Hirayama[11], Fig.1). ; detailed plot for each metal see Bass[32] in 1984-Landolt-Börnstein. The low side of 0.5 in Eq.(38) is of course the beginning of the influence of Grüneisen-Bloch-like form $\rho \propto T^m$, where m is not necessarily 5, but only $m \sim 5$. Thus what T_{room} implied for $\sigma \propto T$ in this paper must be understood to be treating the above range, while $C_{V-\text{lattice}}/T = \text{const}$ keeps generally up to T_{melt} as in Fig.2 of Hirayama[11]. (One interesting point in the latter figures is that a unit of $\hbar\Omega_{\text{ion}}/k_B$ with $Z = 1$ instead of the Debye temperature can be taken another unit temperature.) Also theoretical treatments using the word ‘high temperature’, or even $T \gg \Theta$ must keep these in mind.

Bass et al.(1990)[33] reviewed that Alkali metals show $\rho \equiv 1/\sigma \propto T^2$ at $T \leq 1\text{K}$ and $\rho \propto T$ in regions of $\Theta(\text{Debye}) \leq T \leq T_{\text{melt}}$ (melting point), which gradually tends to show the Bloch-Grüneisen relation $\rho \propto T^5$ in $T \geq 20\text{K}$. As for the theoretical absolute values at 295K, they claim that $|\rho_{\text{calc}}/\rho_{\text{obs}} - 1| \leq 1\%$ in K and Na are reproduced, while in Li this is 180% and in Cs and Rb it is 10 to 20%. On the other hand, in transition metals the situation is very much worse, or no calculations as summarized by Rossiter[25]. There are some computations for transition metals, where e.g. the experimental phonon state density (not for electron) is used as summarized in Rossiter[25], which give a reasonable agreement though accuracy is about the same as our Fig. 1b-upper. Whether $\rho \propto T^5$ or T^2 (often referred to electron-electron scattering regime) is dominant at the very low temperature ranges is of the

current interest. We recall the well-known fact that the elastic scattering of electrons with ions at high temperature range of $T \approx T_{\text{room}}$ is related to large deflection angles $|\theta| \approx \pi$, while in $T \ll T_{\text{room}}$, $|\theta| \ll \pi$ leads to the limiting Grüneisen-Bloch formula of $\sigma \propto T^{-5}$; thus approximately $\sigma \propto T^{-1} \sin^4(\theta/2) \propto T^{-1}(T/\Theta)^{-4}$, namely $\sigma \propto \tau_0(T/\Theta)^{-4} \propto (T/\Theta)^{-5}$, though detailed examination is beyond the scope of the present paper.

10. Conclusions

In our view, the reason why $\text{Cr}(1/\sigma_{\text{obs}} = 129 \text{ n}\Omega \text{ m} = 12.9 \times 10^{-6} \Omega \text{ cm at } T_{\text{obs}} = 295 \text{ K})$ is more resistive than $\text{Cu}(17 \text{ n}\Omega \text{ m}, 4 \text{ s}^{-1}, G=1)$, in fact by 7.6, is simply due to large $G(\text{Cr}, 3\text{d}^5 4\text{s}^1)=6$, i.e. a larger number of equally contributing bands, since $n_{\text{atom}}(\text{Cr})=8.3$ is nearly equal to $n_{\text{atom}}(\text{Cu})=8.5$ (10^{28} m^{-3} unit).

We find in this paper that Eq.(2) for σ and λ using $\tau_0 = \hbar/k_B T$ of Eq.(1) agrees well with the experiments for most of elemental metals, inclusive of semimetals, at room temperature ranges. Though only for the thermal conductivity, even semiconductors of Si and Ge agree with our formulae. Here we adopt that G is the sum of outer electron numbers in the electron configuration with some modifications (e.g. $3\text{d}^{10} 4\text{s}$ is replaced by 4s in Cu). Also $n=n_{\text{atom}}$, namely $Z=1$, and $m^*=m$ are found to be consistent with the σ -observations. These results are found to be, in the words of classical equation of motion for a single electron, $m dV_x/dt = -eE_x - m\nu_{\text{tot}} V_x - \text{drift} = 0$. Here ν_{tot} is the total resistive frequency given by $\nu_{\text{tot}} = \Sigma \nu_i = \frac{1}{\tau_0} G$, where every ν_i for each i -band is assumed equal to $1/\tau_0$.

Three versions of the theoretical derivation of $\tau_0 = \hbar/k_B T$ are considered at the room temperature range. (A) we find that the relaxation time from the Bardeen is $\tau_B = \tau_0 \times (C/E)^{-2}$ (C =deformation ion potential), if we accept the observationally found near-Bohm-Staver relation of $3MC_{\text{tot}}^2 = E_F$ of Eq.(11), where $C_{\text{tot}} = (C_{\text{long}}^{1/3} + 2C_{\text{trans}}^{1/3})^3$ is the averaged total sound speed for each ion of mass M . This takes care of the often claimed assertion that the ion vibration is a single source of the non-zero resistivity. Because $\sigma/\sigma_{\text{obs}} = 1.0 \pm 0.2$ or so as in Fig.1(b)-upper is found for the majority of metals, we better conclude that in fact $(C/E)^{-2}$ should be within that order, or simply unity. (B) we assume $\tau_0 = n_{\text{eff}} S V_F$, where $n_{\text{eff}} = (3.3kT/E_F)n$ is from the steeply decreasing part of the electron Fermi distribution function, and S is the effective collisional area. Here we find $\pi a_0^2 < S < d^2 \equiv n^{-2/3}$, so that because we know $S \approx d^2/2$ from τ_0 , it is not a bad approximation, but also because of its simplicity, it may help for further study with regard to (A) or (C).

As a third derivation of (C), we take a split form of Eq.(21), $\sigma = ne^2 \tau_{\text{cor}}/m$, and Eq.(22) from the classical form of the fluctuation dissipation theorem of Eq.(20). If we assume that the electrons are nearly free as evidenced from the large mean-free-paths, then the wave packet in

the Schrödinger equation takes $\Delta x \Delta p_x = \hbar/2$, which is the minimum uncertainty value, regardless of whether one takes a completely free-atom or a Bloch form. Or similarly $\Delta E_{\text{kin-x}} \Delta t = \hbar/2$ [30].

$$\tau_{\text{cor}} \equiv \frac{\int_0^\infty \langle v_x(0)v_x(t) \rangle dt}{k_B T/m} = \frac{\int_0^\infty \frac{m}{2} \langle v_x(0)v_x(t) \rangle dt}{k_B T/2} \quad (39)$$

$$= \frac{2}{k_B T} \langle \frac{1}{2} m v_x(0)^2 \rangle \langle \Delta t \rangle \quad (40)$$

$$= \frac{2}{k_B T} \langle \Delta E_{\text{kin-x}} \rangle \langle \Delta t \rangle = \frac{2}{k_B T} \frac{\hbar}{2} = \frac{\hbar}{k_B T} \quad (41)$$

Here Eq.(39) \equiv Eq.(22), Eq.(40) takes the average of the autocorrelation function, and in Eq.(41), $\Delta E_{\text{kin-x}}$ is the fluctuating kinetic energy of electrons. If we use $\Delta E_{\text{kin-x}} \Delta t = \Delta p_x \Delta x = \hbar/2$, the same result will hold. This method again explicitly uses no ion-vibrations (of course, Eq.(11) counts). The method (C) involves no adjustable parameters, matches the observations quite well as Fig.1(b)-upper, and hence is perhaps a most reliable.

I thank Profs. Noboru Miura, Toru Suemoto, and Hiroshi Ezawa for discussion.

Appendix A: Derivation of Conductivity from the Boltzmann Equation

This appendix is only to recall the well-known derivation of Eq.(2) for σ without specifying τ and using $G=1$, electron number density $n = n_{\text{atom}}$ (Sect.4), and $m = m^*$ (Sect.5). Thus we derive $\sigma = j_x/E_x$ for a single band as preparation for multi-band metals: e.g. each one of five ‘d’ or one ‘s’ band in $\text{Cr}(3\text{d}^5 4\text{s}^1)$. We rewrite the current density as

$$j_x = -e \int v_x f d\mathbf{k}_1 = -e \int \frac{\hbar k_x}{m} (f - f_0) d\mathbf{k}_1, \quad (A1)$$

using $d\mathbf{k}_1 \equiv g_e d\mathbf{k}/(2\pi)^3 @ (g_e = 2 \text{ is from electron spin})$, $m v_x = \hbar k_x$, and f_0 and f are unperturbed and perturbed Fermi distribution function, respectively. For convenience, to the last term we added $-\int_{-\infty}^\infty \frac{\hbar}{m} k_x f_0 d\mathbf{k}_1 = 0$, because $k_x f_0$ is an odd function of k_x , and hence vanishes.

Given the electric field E_x in the x direction, the ‘steady’ Boltzmann equation from $\partial f/\partial t - eE_x \partial f/\hbar \partial k_x = (\partial f/\partial t)_{\text{coll}}$ is

$$-eE_x \frac{\partial f_0}{\hbar \partial k_x} = -\frac{f - f_0}{\tau}, \quad (A2)$$

where we adopted the relaxation time approximation for the collision term $(\partial f/\partial t)_{\text{coll}}$. First we insert $(f - f_0)$ of Eq.(A2) into Eq.(A1) and assume a \mathbf{k} -independent τ as in Eq.(1). We thus obtain $\sigma = j_x/E_x$ in the Drude form as

$$\frac{\sigma}{e^2 \tau/m} = - \int k_x \frac{\partial f_0}{\partial k_x} d\mathbf{k}_1 = \int f_0 \frac{d\mathbf{k}}{4\pi^3} = n. \quad (A3)$$

Partial integration over dk_x within the primitive cell leads to the second equality of Eq.(A3) ; for $f = f(k_x, k_y, k_z)$, $(\int_{-\infty}^{\infty} k_x \frac{\partial f}{\partial k_x} dk_x) dk_y dk_z = -(\int_{-\infty}^{\infty} f dk_x) dk_y dk_z$, and $k_x f \rightarrow 0$ for $k_x \rightarrow \pm\infty$ due to more rapidly changing f than the change of k_x . The final equality of Eq.(A3) leads to n , where $n = \int f D(E) dE = \int f_0 d\mathbf{k} / 4\pi^3$ ($D(E)$ is the state density).

Because of the factor $\partial f_0 / \partial k_x$ in Eq.(A3), not only a band, where the state density does not extend beyond the Fermi energy, does not contribute to σ such as $3d^{10}$ of Cu (see e.g. Ibach and Lüth[2], Fig.7.12, left), but also only electrons having the energy of $E_F \pm 2k_B T \approx E_F$ are contributing to σ (E_F =Fermi energy=2-7eV for $Z=1$). For the same reason, even if τ is dependent upon k , this must come from $\tau = \tau(k \approx k_F)$.

Since we used coordinates of $f = f(k_x, k_y, k_z)$, the result, namely n , is the same as given in Eq.(A3) even for the non-free electron model such as non-hyperbolic bands. In the latter the surface area is left unknown,

though useful for some other problems. Note that the departure from $d\mathbf{k} = 4\pi k^2 dk = D_{\text{free}}(E_F) dE$ is by a multiple factor of $D(E_F) / D_{\text{free}} = 1.2-1.6$ from the tabulation of $D(E_F)$ for each metal in Moruzzi et al [16], and that the model appears to change the value of E_F .

We adopted $(\partial f / \partial t)_{\text{coll}} = -(f - f_0) / \tau$ as the collision term. This can be understood by $f = f_0 - (\partial f / \partial t)_{\text{coll}} \tau$ of the Taylor expansion. Therefore, though it is conventionally called ‘relaxation time approximation’, in reality, it can be anything that satisfies the linear Taylor expansion, such as the correlation time τ_{cor} as shown in Sect.9. The correlation time may well be more appropriate since we assumed $\partial f / \partial t = 0$ in Eq.(A2). Besides, the linear Taylor expansion is readily shown accurate enough, since the required electric field for non-linearity is quite large [e.g. Grosso and Parravicini[34] below their Eq.(11.30b)].

The rough derivation above may be sufficient for the discussion in the text.

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